Marine Pollution Bulletin 71 (2013) 74–82

Contents lists available at SciVerse ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Tracing organic matter removal in polluted coastal waters via floating bed phytoremediation

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ARTICLE INFO

Keywords:
Phytoremediation
Floating beds
Organic pollution
Fluorescence EEM
Parallel factor analysis
Sesuvium portulacastrum

ABSTRACT

Organic matter removal by cultured *Sesuvium portulacastrum* in constructed floating beds was studied during a 20 day greenhouse experiment and an 8 month field campaign in the polluted Yundang Lagoon (southeastern China). Experiments were traced via dissolved organic carbon (DOC) concentration, fluorescence excitation–emission matrix and absorption spectroscopy. Two 'terrestrial' humic-like, one 'marine' humic-like and one protein-like components were identified by parallel factor analysis. The 'terrestrial' humic-like and protein-like components, DOC and absorption coefficient (a280) decreased during the greenhouse experiment. The intensities of four fluorescence components were all reduced during the field experiment. These results demonstrate the clear potential of floating bed phytoremediation techniques for reducing organic pollution degree in brackish environments. The rhizosphere may play an important role during phytoremediation. Our results show that spectrophotometric measurements such as fluorescence provide a useful tool for examining the removal of different organic moieties during various bioremediation processes.

1. Introduction

Aquatic pollution is a significant problem globally, primarily due to the discharge of large amounts of wastewater derived from agricultural (i.e. manure), industrial and municipal activities (Baker, 2002; Baker et al., 2003, 2004; Zhuo et al., 2010). The traditional physical and chemical remediation techniques for such pollution issues are generally expensive and also in some instances have the potential to introduce secondary pollution (Meagher, 2000; Shen et al., 2004). Recently, phytoremediation has been highlighted as an effective way to reduce the content of organic matter, nutrients and heavy metals in polluted waters and is commonly regarded as a green technology (Hadad et al., 2006; He et al., 2008; Valipour et al., 2009). Phytoremediation is a novel bioremediation technology in which plants are utilized to remove or degrade complex environmental pollutants (Cunningham et al., 1997; Meagher, 2000; Stottmeister et al., 2003). This technique is also cost effective, ecologically advantageous, and is easily accepted, in fact often welcomed by the general public due to its significant improvement of the anthropogenically impacted landscape (Trapp and Karlson, 2001).

In polluted coastal and brackish waters, the plantation of large-sized seaweeds, mangrove and other salt-tolerant plants has been developed to restore disturbed habitats (Wilcox and Whillans, 1999; He et al., 2008; Agunbiade et al., 2009). However, some ecological concerns may arise, e.g. the introduction of smooth cordgrass (*Spartina alterniflora* Loisel) along the Chinese southeast coast has led to a serious invasive species issue (Wang et al., 2006). To try to avoid this scenario, phytoremediation technology utilizing floating beds of aquatic plants has been developed (Huett et al., 2005; Zhang, 2010). By culturing a highly salt-tolerant euryhalophyte plant, *Sesuvium portulacastrum* (Messedi et al., 2004) in floating beds in greenhouse with polluted media, Zhang (2010) found that total nitrogen (TN) and total phosphorus (TP) concentrations could be efficiently reduced (62.2% and 51.4% reduction compared with the initial contents, respectively). When such a technique was applied in the highly polluted Yundang Lagoon, southeastern China (Zhuo et al., 2010), the monthly removal amount for nitrogen and phosphorus was 1.1 and 0.2 g/m^2, respectively (Zhang, 2010). Although the technique has demonstrated great potential for reducing the nutrient content in polluted environments, the removal effect and possible mechanism for organic matter (OM) mitigation has not yet been examined. This issue is also important as organic pollution is still a significant problem in brackish and coastal waters (Spencer et al., 2007a; Guo et al., 2010; Zhuo et al., 2010) and so is a topic of great relevance to coastal cities around the world.

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0025-326X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2013.03.032

Traditionally, the general indicators used to examine the variation of organic substances during phytoremediation are the commonly used water quality metrics such as chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Calheiros et al., 2007). These are indirect indices that are unable to provide the true concentration or give compositional information concerning the complex and heterogenic nature of organic substances in aquatic environments. Hence, these indices are not ideal to investigate the removal mechanism for dissolved organic pollutants during phytoremediation. Recently, excitation emission matrix (EEM) fluorescence spectroscopy has received a great deal of attention with respect to the characterization of dissolved organic matter (DOM) in aquatic environments (Coble, 2007; Kowalczuk et al., 2009; Fellman et al., 2010). Fluorescence EEM's can provide a large amount of information that can be objectively identified using a multivariate statistical tool called parallel factor analysis (PARAFAC) (Bro, 1997; Stedmon et al., 2003; Stedmon and Bro, 2008). The peak positions and F_{max} of the individual fluorescent components identified can be used for tracing the qualitative and quantitative variation of DOM (Stedmon and Markager, 2005; Yamashita et al., 2008; Fellman et al., 2010; Guo et al., 2011). Additionally, UV–Visible absorption spectroscopy is another spectroscopic approach that can also provide quantitative and qualitative information in relation to DOM (Guo et al., 2007; Helms et al., 2008; Spencer et al., 2010).

Therefore, EEM-PARAFAC and absorption spectroscopy provide powerful tools for assessing the degradation, degree of removal and mechanism of removal for organic substances during floating bed phytoremediation in polluted aquatic environments. In this study, we conducted a 20-day greenhouse incubation experiment by culturing shoreline purslane (*S. portulacastrum*) in polluted media prepared by mixing sewage water with seawater. A large-scale field remediation campaign was also undertaken using the same floating bed phytoremediation technique, in the inner bay of the Yundang Lagoon (Xiamen, China). The main objective was to evaluate the remediation effects for bulk organic matter via DOC concentration and different organic moieties determined via spectrophotometric techniques (fluorescence EEM-PARAFAC and absorption spectroscopy) in brackish polluted systems. The possible removal mechanism for DOM via the phytoremediation method was also examined. The overarching goal of this research was to examine the potential for utilizing sensitive spectrophotometric techniques to observe the remediation and purification effects for different organic moieties via phytoremediation.

2. Materials and methods

2.1. Yundang Lagoon

Yundang Lagoon is a coastal eutrophic shallow brackish lake located on Xiamen Island, southeast of China (Fig. 1). The total area of the lagoon is 1.5 km^2, with an average depth of approximately 2.5 m. It is typically divided into three parts: the Main Canal, Inner Lake and Outer Lake. The salinity range is typically 12–31, with a mean value of 27 (Zhuo et al., 2010). In the past three decades, Yundang Lagoon was highly polluted due to the discharge of municipal sewage from many outlets around the lagoon and the weak or even stagnant hydrodynamics in this enclosed environment. In the early 1990s, an engineering scheme was adopted to enhance the flushing within the lagoon with the goal of alleviating the degree of pollution. In brief, relatively clean seawater from the outer bay flows into the lagoon during the high tide period through a diversion canal inlet and the polluted lagoon water flows out from the outlet at low tide. Even so, the degree of organic and nutrient pollution within the lagoon is still severe, as there are still numerous sewage discharges into the lagoon, mainly from the upstream Main Canal.

2.2. Greenhouse incubation experiment

The plant used for the phytoremediation experiment was *S. portulacastrum*, a species belonging to the *Aizoaceae*, and it is a sprawling perennial herb that grows in coastal areas throughout much of the world. Each individual plant was grown for 3 months in a greenhouse prior to use in this incubation study.

The incubation experiments were conducted from the 19th November to the 9th December 2009 in a greenhouse at 28 °C near the Yundang Lagoon. The culture media was prepared by mixing original sewage water from the Yundang Wastewater Treatment Plant (WWTP) (see location in Fig. 1) with seawater from the outer bay at a ratio of 1:4. The salinity was adjusted to 27, the average salinity level of the lagoon, and 16 L of media were added to four individual transparent tanks (30 cm × 25 cm × 20 cm), with two tanks as a control group and the other two tanks as the incubation group. All tanks were wrapped completely with aluminum foil to avoid the growth of phytoplankton. The media was recycled continuously throughout the experiment (Fig. 2). Ten *S. portulacastrum* individuals were planted in each incubation tank after been soaked in Milli-Q water for 2 days to remove any freshwater algae species attached to the roots. All *S. portulacastrum* individuals grew well during the whole incubation process, with an average increase of 8.5% for the weight of individuals at the end of the 20 days.

Water samples were collected from each tank at the start and every 5 days throughout the experiment. Sub-samples for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) measurements were immediately filtered through precombusted (450 °C, >5 h) 0.7 μm Whatman GF/F glass fiber filters and stored at 4 °C in the dark after being acidified to pH < 2 using concentrated HCl. Sub-samples for fluorescence and absorption analysis were filtered using 0.2 μm pre-cleaned Millipore polycarbonate filters, stored at 4 °C in the dark and analyzed within 2 days of collection.

2.3. Field phytoremediation campaign in the Yundang Lagoon

In order to verify the practicality and remediation effect of such a phytoremediation technique in field environments, 10,000 m^2 of floating beds cultured with *S. portulacastrum* were paved in the north channel of the Inner Lake of the Yundang Lagoon from July 2009 to March 2010. Three sampling sites were setup in this phytoremediation demonstration area (Fig. 1): Site A located in the polluted Main Canal; Sites B and C represented the sample before and after restoration area, respectively. Water samples were collected from these sites during the fast-growing phase (December, 2009) and stationary phase (March, 2010) of the growth period of *S. portulacastrum*. The pretreatments for these samples followed the protocols of the greenhouse incubation experiment (see Section 2.2).

2.4. EEM measurement and PARAFAC modeling

EEM fluorescence spectra were obtained using a Cary Eclipse (Varian, Australia) fluorometer equipped with a 150 W Xe arc lamp. The emission spectra were scanned every 2 nm at wavelengths from 300 to 600 nm, with excitation wavelengths of 250–450 nm at 5 nm intervals (Guo et al., 2011). The spectra of each sample was calibrated with the Raman peak of Milli-Q water (Stedmon and Markager, 2005) and subtracted Raman-normalized spectra of Milli-Q water which was scanned on the same day. Highly absorbing samples were diluted with Milli-Q water prior to analysis to avoid inner-filter effects (IFE) following the method